the marked distortion of the tribenzylaluminum molecule.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. tribenzylaluminum, 14994-03-7.

Supplementary Material Available: Tables containing hydrogen atom positional parameters anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen, C–C bond lengths and C–C–C angles in the aromatic ring, and observed and calculated structure amplitudes (12 pages). Ordering information is given on any current masthead page.

Positively Charged Ligands. The Structure and Bonding of Coordinated Sulfonium Cations: Synthesis and Crystal and Molecular Structure of $Mo(CO)_4[PPh_2(CH_2)_2SMe_2]^+BF_4^-$

Richard D. Adams* and Mahmoud Shiralian

Department of Chemistry
Yale University
New Haven, Connecticut 06511

Received March 9, 1982

Summary: The complex $Mo(CO)_4[PPh_2(CH_2)_2SMe_2]^+BF_4^-$, I, has been synthesized by alkylation of the lone pair of electrons on the sulfur atom in $Mo(CO)_4[Ph_2P(CH)_2SMe]$, II. Single-crystal X-ray structural analysis of both I and II have been performed. For I: space group $P2_1/c$; $a = 16.928$ (5) Å, $b = 21.786$ (12) Å, $c = 13.900$ (9) Å, $\beta = 106.38$ (4)°; $Z = 8$, ρ(calcd) = 1.540 g/cm^3. For II: space group $P2_12_12_1$; $a = 8.150$ (6) Å, $b = 14.229$ (6) Å, $c = 17.209$ (9) Å; $Z = 4$, ρ(calcd) = 1.559 g/cm^3.

In 1976 we reported the first example of a coordinated sulfonium cation.[1] An X-ray structural analysis of one of these complexes, $[MeC_5H_4Mn(CO)_2SMe_2Et]^+BF_4^-$, showed an unusually short metal–sulfur bond distance.[2] High-frequency stretching of the carbonyl ligands indicated that the sulfonium ligand was strongly electron withdrawing, and a bonding model which included a significant amount of d_π–d_π back-bonding was proposed.[2] Since then other examples of complexes containing positively charged ligands have been reported.[3-5] Interestingly the complex, $C_5H_5Mo(CO)_2[\overline{PNMe(CH_2)_2N}Me]$, in which the phosphorus atom of the cyclic, positively charged phosphenium ligand, $(PNMe(CH_2)_2NMe)^+$, is coordinated to the metal atom, showed an unusually short metal–phosphorus bond distance. This was also interpreted in terms of a π back-bonding effect and was supported by MO calculations.[5b]

We have now synthesized the chelate complex $Mo(CO)_4[PPh_2(CH_2)_2SMe_2]^+BF_4^-$, I via alkylation of the lone pair of electrons on the sulfur atom in the chelate complex $Mo(CO)_4[PPh_2(CH_2)_2SMe]$, II.[6,7] In a typical preparation 0.100 g (0.213 mmol) of II and 0.100 g (0.675 mmol) of $Me_3O^+BF_4^-$ were vigorously stirred at room temperature, under nitrogen in CH_2Cl_2 solvent (40 mL) for 2 days. The solution was filtered, and I was crystallized by addition of hexane to give white crystals, yield 65%.[7] This pseudooctahedral complex contains the chelating ligand $Ph_2P(CH_2)_2SMe_2^+$ in which the sulfur atom is formally positively charged. It is hoped that a structural analysis of I would provide further evidence about the nature of the metal–sulfur bond and its effect on the bonding of the other ligands to the metal atom. Thus, single-crystal x-ray structural analyses of both I[8] and II[9] have been performed for comparative purposes. Both will be described briefly here.[10]

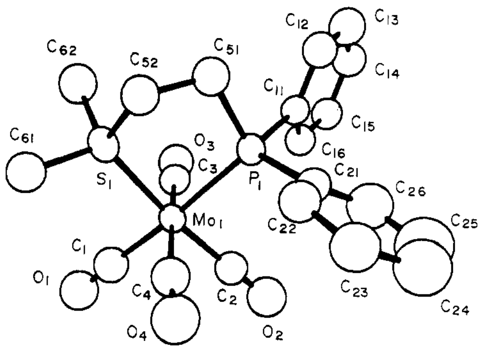

Figure 1. An ORTEP diagram showing 50% electron density probability ellipsoids of one of the two independent cations of $Mo(CO)_4[PPh_2(CH_2)_2SMe_2]^+$ in the crystal of $Mo(CO)_4[PPh_2(CH_2)_2SMe_2]^+BF_4^-$.

Table I. Selected Internuclear Separations (Å) with Esds in $Mo(CO)_4[PPh_2(CH_2)_2SMe_2]^+BF_4^-$, I and $Mo(CO)_4[PPh_2(CH_2)_2SMe]$, II

	I			
atoms	molecule 1	molecule 2	av	II
Mo-S	2.420 (1)	2.405 (1)	2.412	2.547 (1)
Mo-P	2.485 (1)	2.520 (1)	2.502	2.521 (1)
Mo-C(trans S)	1.943 (5)	1.945 (6)	1.944	1.957 (4)
Mo-C(trans P)	1.992 (6)	1.958 (5)	1.975	1.977 (4)
Mo-C(av trans COs)	2.005 (5)	1.988 (5)	1.997	2.018 (4)
S-C(av Me)	1.816 (6)	1.822 (6)	1.819	1.778 (5)

An ORTEP drawing of I is shown in Figure 1. The compound crystallizes with two formula equivalents in the asymmetric crystal unit. Structurally, both molecules are very similar. Table I presents selected bond distances for both independent cations of I, their averaged values, and the corresponding bond distances in II. In comparisons with II, we will use the averaged values of I.

---

(1) Adams, R. D.; Chodosh, D. F. *J. Organomet. Chem.* **1976**, *120*, C39.

(2) Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1978**, *100*, 812.

(3) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1978**, *100*, 336.

(4) (a) Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. (b) Bennett, D. W.; Parry, R. W. *Ibid.* **1979**, *101*, 755.

(5) (a) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230. (b) Hutchins, L. D.; Paine, R. T.; Campana, C. F. *Ibid.* **1980**, *102*, 4521.

(6) Ross, E. P.; Dobson, G. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2363.

(7) ^{1}H NMR of I (CD_2Cl_2): δ 7.51 (m, Ph), 4.03 (dt, CH_2, $J_{P-H} = 21.6$ Hz, $J_{H-H} = 6.2$ Hz), 3.52 (s, Me), 2.74 (dt, CH_2, $J_{P-H} = 6.8$ Hz, $J_{H-H} = 7.3$ Hz).

(8) For I: space group $P2_1/c$, No. 14; $a = 16.928$ (5) Å $b = 21.786$ (12) Å, $c = 13.900$ (9) Å, $\beta = 106.38$ (4)°; $Z = 8$, $\rho_{(calcd)} = 1.540$g/cm^3. Least-squares refinement on 4912 reflections, $F_0^2 \geq 3.0\sigma(F^2)$ produced the final residuals $R_1 = 0.700$ and $R_2 = 0.084$.[10] Hydrogen contributions were not included in this analysis. Only atoms heavier than fluorine were refined anisotropically.

(9) For II: space group $P2_12_12_1$, No. 19; $a = 8.150$ (6) Å, $b = 14.229$ (6) Å, $c = 17.209$ (9) Å; $Z = 4$, $\rho_{(calcd)} = 1.559$g/cm^3. Least-squares refinement on 1699 reflections, $F^2 \geq 2.0\sigma(F^2)$ produced the final residuals $R_1 = 0.025$ and $R_2 = 0.022$. Hydrogen atom contributions were included in the structure factor calculations, but they were not refined. All nonhydrogen atoms were refined anisotropically.

(10) Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. Both structures were solved by the heavy-atom method. All calculations were done on a Digital PDP-11/45 computer using the programs of the Enraf-Nonius SDP program library (version 16).

0276-7333/82/2301-0883$01.25/0

First and foremost, it is observed that the positively charged sulfur atom is formally coordinated to the molybdenum atom. Second, the approximately octahedral coordinating geometry about the metal atom is confirmed. The molecular structure of II is very similar to that of I; however, its metal–sulfur bond distance at 2.547 (1) Å is 0.135 Å longer than that in I, 2.412 Å. The molybdenum–carbon distance to the carbonyl ligand trans to the molybdenum–sulfur bond at 1.944 Å is slightly shorter than the corresponding distance of 1.957 (4) Å observed in II. The shortness of the metal–sulfur bond in I implies that it is stronger than that in II, but this does not produce an observable weakening of the bond trans to it as would be expected on the basis of the π back-bonding theory.[11,12] However, structural trans effects are not usually large and in some cases have not been observed when expected.[13] In addition, it has been proposed that trans effects are also influenced by σ bonding,[14] and a ligand with a weak σ inductive effect would lead to a strengthening of the bond trans to it. If sufficiently weak, this might completely offset the weakening effect caused by the π back-bonding. Bond distances to the ligands cis to the Mo–S bonds are similar in both I and II. Thus, there is also no observable structural cis effect.

Infrared spectra show that the absorption frequencies of the carbonyl ligands in I are significantly higher than those in II.[15] This further supports the notion that the coordinated sulfonium group in I is strongly withdrawing electron density from the metal atom. π back-bonding would seem to be the most likely mechanism.

The shortness of the molybdenum–sulfur bond in I suggests that it is thermodynamically quite stable; however, reactivity studies show that in reactions with nucleophiles, it is kinetically labile. For example, under an atmosphere of carbon monoxide, I reacts over a period of 8 h. in CH_2Cl_2 solvent to form $Mo(CO)_5[PPh_2(CH_2)_2SMe_2]^+BF_4^-$.[16] Over the same period of time, II shows no significant reaction with CO. Parry showed that the cationic complex $Fe(CO)_4[PNMe(CH_2)_2NMe]^+$ was also unusually reactive in nucleophilic substitution reactions, but for this complex it was the ancillary carbonyl ligands and not the positively charged ligand which was replaced.[4b]

In summary, it has been found that the coordinate bond between a metal atom and sulfonium cation is unusually short. Interestingly, this ligand does not produce a significant structural trans-weakening effect. Further studies of the structure, bonding and reactivity of this unusual coordinate bond are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the Alfred P. Sloan Foundation for a fellowship to R.D.A.

Supplementary Material Available: Complete tables of structure factor amplitudes, fractional atomic coordinates, bond distances, and bond angles are available for both crystal structures (39 pages). Ordering information is given on any current masthead page.

---

[11] Appleton, T. G.; Clark, H. D.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

[12] Plastas, H. F.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

[13] Vahrenkamp, H. *Chem. Ber.* **1971**, *104*, 449.

[14] Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

[15] IR (CH_2Cl_2): for I ν(CO) 2048 (s), 1965 (m, sh), 1943 (vs, br) cm^{-1}; for II ν(CO) 2023 (ms), 1913 (s), 1869 (ms) cm^{-1}.

[16] For $Mo(CO)_5[PPh_2(CH_2)_2SMe_2]^+BF_4^-$; IR ($CH_2Cl_2$) ν(CO) 2075 (ms), 1996 (w), 1946 (vs, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (m, Ph), 3.19 (br, CH_2), 2.93 (s, Me), 2.87 (br, CH_2); yield 88%.

Homogeneous Activation of the C–H Bond. Formation of Phenylsiloxanes from Benzene and Silicon Hydrides

Wayne A. Gustavson, Paul S. Epstein, and
M. David Curtis*

Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48109

Received March 5, 1982

Summary: Pentamethyldisiloxane reacts with benzene under catalysis by Vaska's compound to yield phenylsiloxanes and other redistribution products. The compound $Ir(Ph)(CO)L_2$ (L = Ph_3P) reacts with pentamethyldisiloxane in a very unusual fashion to give a series of methylsiloxane oligomers end-capped with one or two phenyl groups.

Homogeneous activation of the C–H bond to substitution of hydrogen by other functionalities is one important goal of current chemical research. There are now a goodly number of reports which describe the reactions of metal complexes with C–H bonds to give insertion products of the type M(H)R or M(H)Ar (R = alkyl, Ar = aryl).[1] However, we know of only one report which describes a catalytic activation–substitution, other than simple H/D exchange, on a C–H bond. That is the brief description by Parshall of the reaction of benzene with triethylaluminum in the presence of Cp_2NbH_3 to yield phenyldiethylaluminum.[2,3] We wish to report the second such activation–substitution of an aromatic C–H bond: the reaction of benzene with silyl hydrides in the presence of iridium(I) complexes to give phenylsilanes.

The activity of some group 8 metal complexes, including those of Ir, Rh, Pt, and Pd, for the catalyzed oligomerization of tetraalkyldisiloxanes (eq 1) has been described.[4]

$$(n+1)(HMe_2Si)_2O \xrightarrow{[cat.]} nMe_2SiH_2 + \underset{E'D_nE'}{HMe_2Si(OSiMe_2)_nOSiMe_2H} \quad (1)$$

In effect, the oligomerization reaction represents a catalyzed exchange of SiO groups for H in the Si–H bond (referred to as an SiO/H exchange). Further investigation[5–7] has revealed that slower Me/H and SiO/Me exchanges also occur in these systems, resulting in complex mixtures. For example, when pentamethyldisiloxane, $Me_3SiOSiMe_2H$, was stirred in benzene with 2 mol % of Vaska's complex $L_2(CO)IrCl$ under N_2 at 60 °C, the

---

[1] The following list of leading references is representative: (a) Parshall, G. W. *Catalysis* (*London*) **1977**, *1*, 335. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; pp 123–128. (c) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (d) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950. (e) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (f) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–188. (g) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (h) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *Ibid.* **1977**, *99*, 7870.

[2] Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

[3] Metal ions which are strong Lewis acids, e.g., Pd^{2+} will, in the presence of oxygen, catalyze the coupling of arenes to biaryls etc.[1a,b,f] The mechanisms of these reactions are not well documented, but probably σ-arylmetal complexes are formed via Friedel–Crafts type reactions (see ref 1b,f). These electrophilic substitutions are considered outside the scope of the "insertion" type discussed here.

[4] Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362.

[5] Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213–255.

[6] Gustavson, W. A.; Bell, L. G.; Curtis, M. D., to be submitted for publication.

[7] Gustavson, W. A.; Epstein, P. S.; Curtis, M. D., to be submitted for publication.